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Beaujean, Pierre

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Theoretical study of the second-order nonlinear optical properties of oxazine derivatives

Pierre Beaujean, Aurélie Plaquet and Benoît Champagne

Laboratory of Theoretical Chemistry — UCPTS — UNamur (61, Rue de Bruxelles, B-5000 Namur)

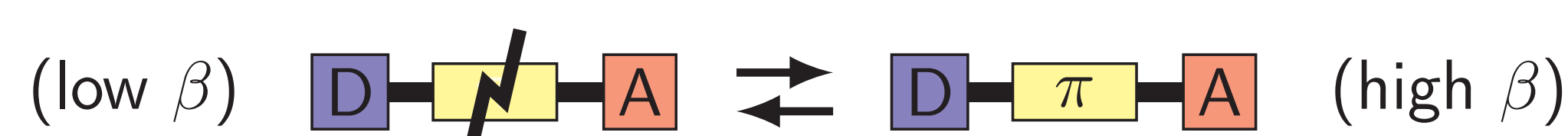
Introduction

- *Molecular switches*: molecules showing large property variations in response to an external stimulus.¹
- Triggering via irradiation of the molecule with a laser at given frequencies.
- The interaction between the dipole moment, $\vec{\mu}$, and the electric field, \vec{E} , is the dominant term in the interaction between matter and electromagnetic field. It can be described using a Taylor series, as

$$\vec{\mu}(\vec{E}) = \vec{\mu}_0 + \vec{\alpha} \vec{E} + \frac{1}{2} \vec{\beta} \vec{E}^2 + \dots$$

where $\vec{\alpha}$ and $\vec{\beta}$ are the polarizability and the first hyperpolarizability²

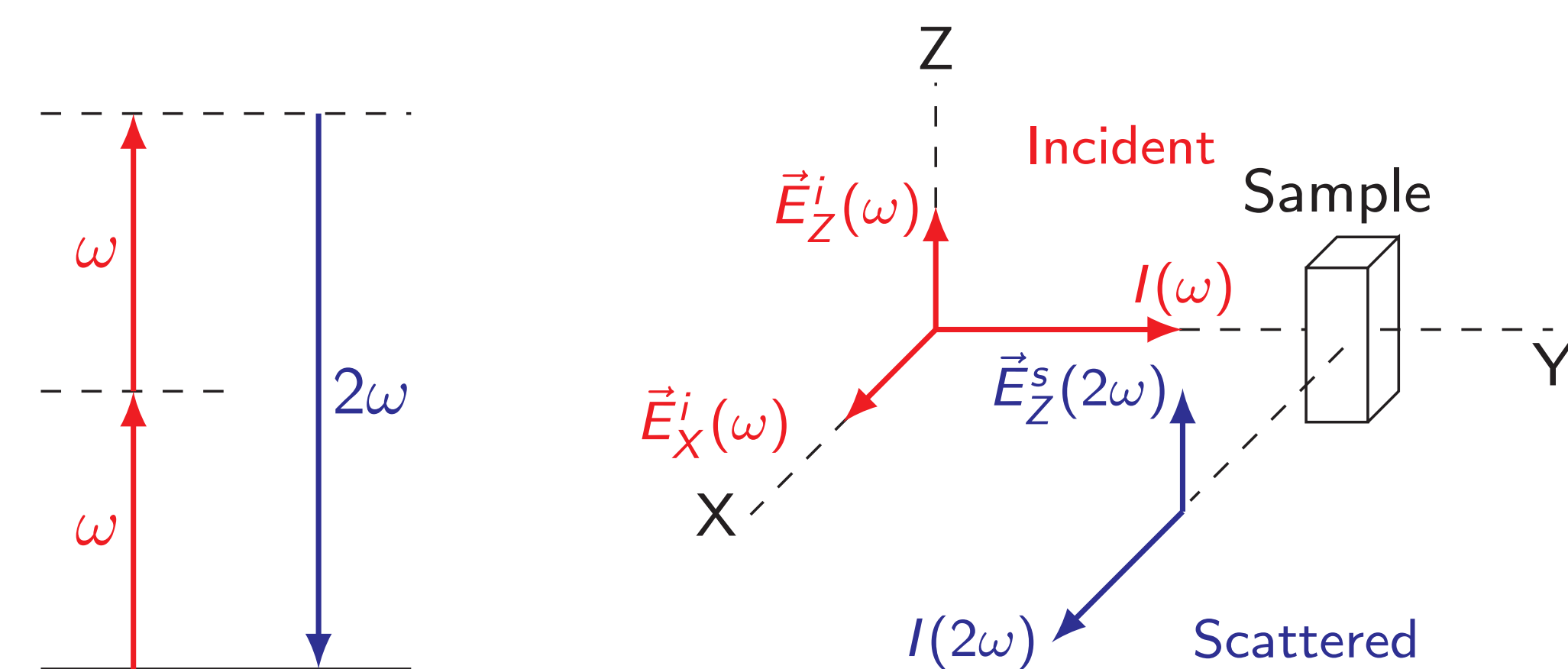
- π -conjugated compounds (terminated by a donor and an acceptor): trigger can modify or even break the conjugation path, resulting in a large change of $\vec{\beta}$.



Those are called *second-order NLO switches*³

- Usage in data storage, imaging microscopy and optical communication

Hyper Rayleigh Scattering (HRS)



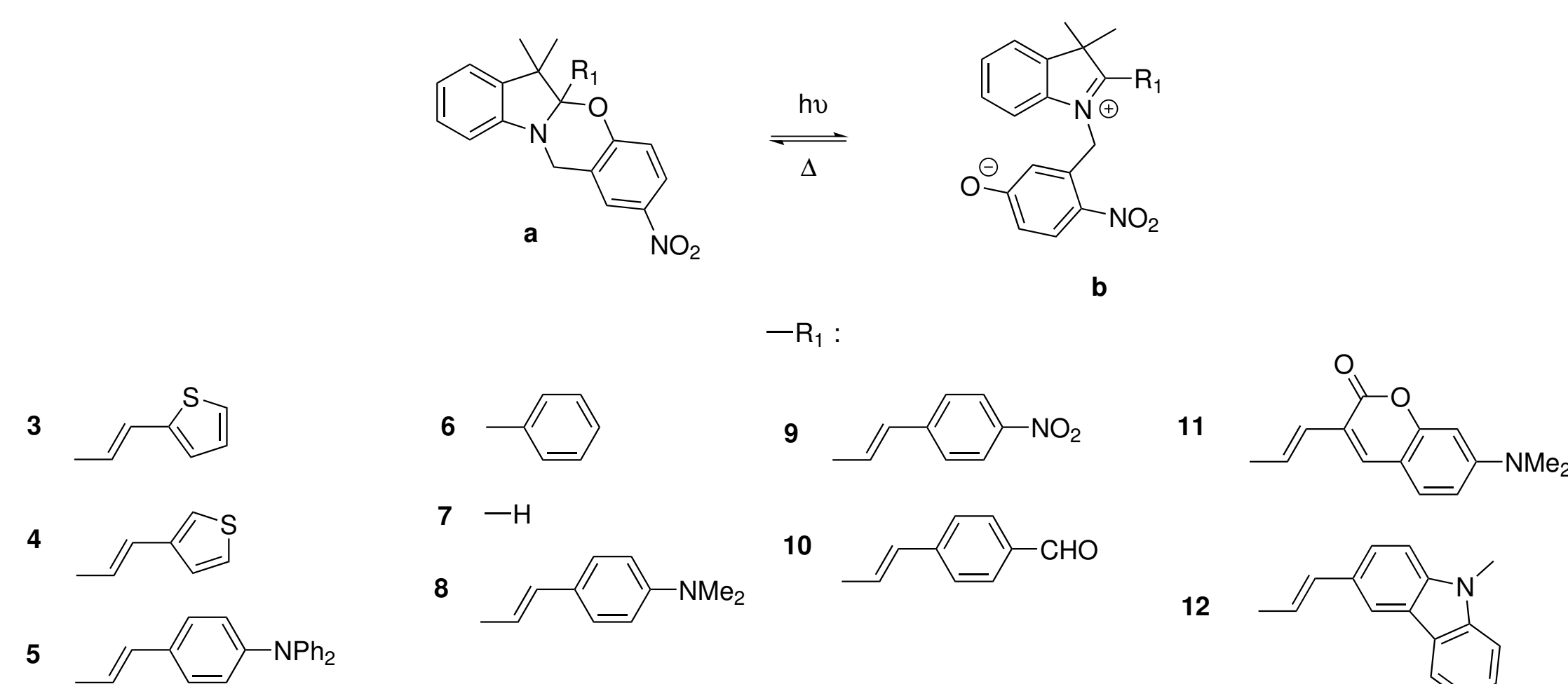
- HRS: nonlinear elastic scattering phenomenon where a molecule illuminated with photons of frequency ω scatters photons of frequency 2ω .
- Measurement at 90° and scattered beam vertically polarized. $I(2\omega) \propto \langle \beta_{ZZX}^2 \rangle$ (if incident beam polarized horizontally) or $\propto \langle \beta_{ZZZ}^2 \rangle$ (if polarized vertically).
- Determination of the full HRS response (β_{HRS}) and depolarization ratio (DR):

$$\beta_{HRS} = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZZX}^2 \rangle} \quad DR = \frac{\langle \beta_{ZZZ}^2 \rangle}{\langle \beta_{ZZX}^2 \rangle}$$

DR gives information on the geometry of the chromophore

Goals and results

Objective: study a new family of NLO switches, the benzo[1,3]oxazines with donor and attractor substituents.



3-6, 8 and 11-12 have recently been synthesized by Raymo and co-workers.⁴ Comparison with value of reference compounds:⁵



Closed (a)						Open (b)					
β_{HRS}	DR	β_{HRS}	DR	Contrast		β_{HRS}	DR	β_{HRS}	DR	Contrast	
					ratio						ratio
1	1427	4.82	12637	4.64	8.86	7	725	3.12	1888	3.73	2.60
2	697	3.31	6833	3.17	9.80	8	1934	5.12	13682	5.31	7.07
3	914	3.94	4292	5.95	4.70	9	1432	3.05	1888	2.49	1.32
4	895	3.91	3261	5.96	3.64	10	1066	2.88	2161	4.20	2.03
5	1704	3.82	17705	5.21	10.39	11	3415	4.64	17236	4.63	5.05
6	828	3.40	1726	3.64	2.09	12	1462	4.52	10708	4.82	7.33

Table: IEF-PCM/TDHF dynamic first hyperpolarizabilities (β_{HRS} , a.u.) as well as the β_{HRS} (open) / β_{HRS} (closed) contrast ratios.

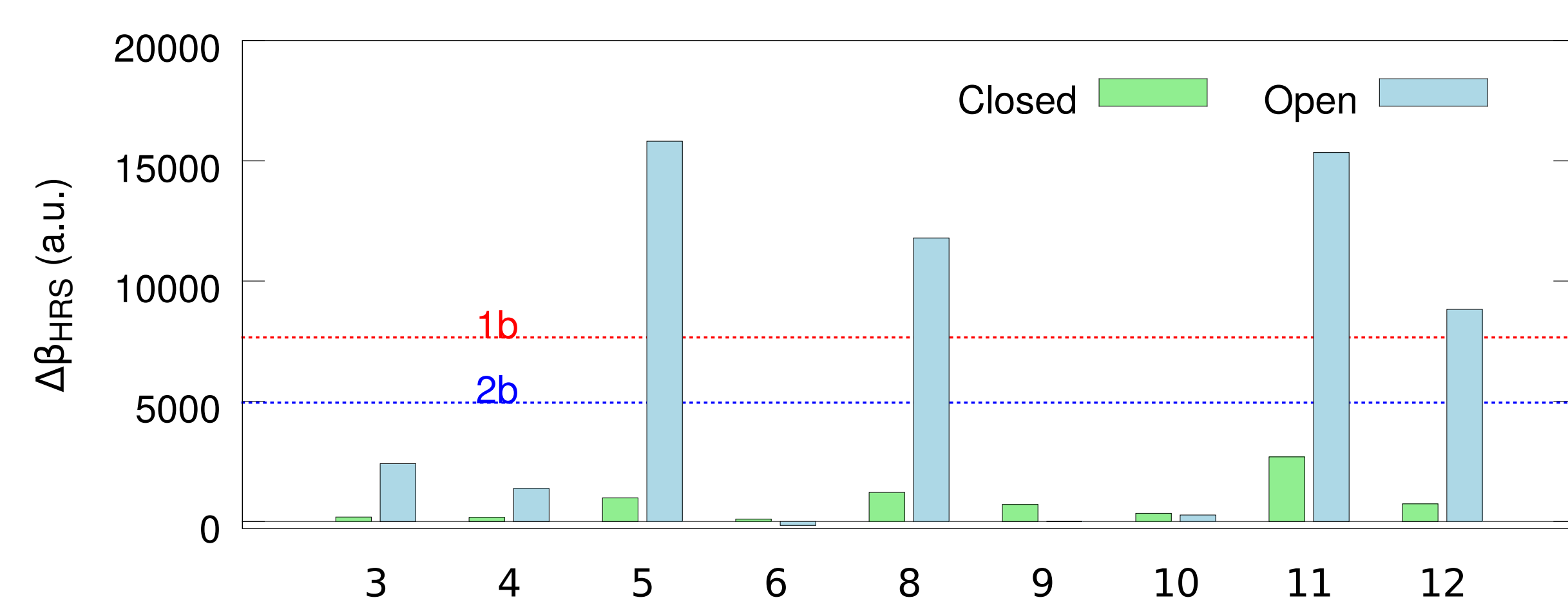


Figure: Substituent effect on the dynamic β_{HRS} estimated by the difference between the dynamic β_{HRS} response of the different compounds and that of **7** ($R_1=H$), taken as reference ($\Delta\beta_{HRS} = \beta_{HRS} - \beta_{HRS}^7$)

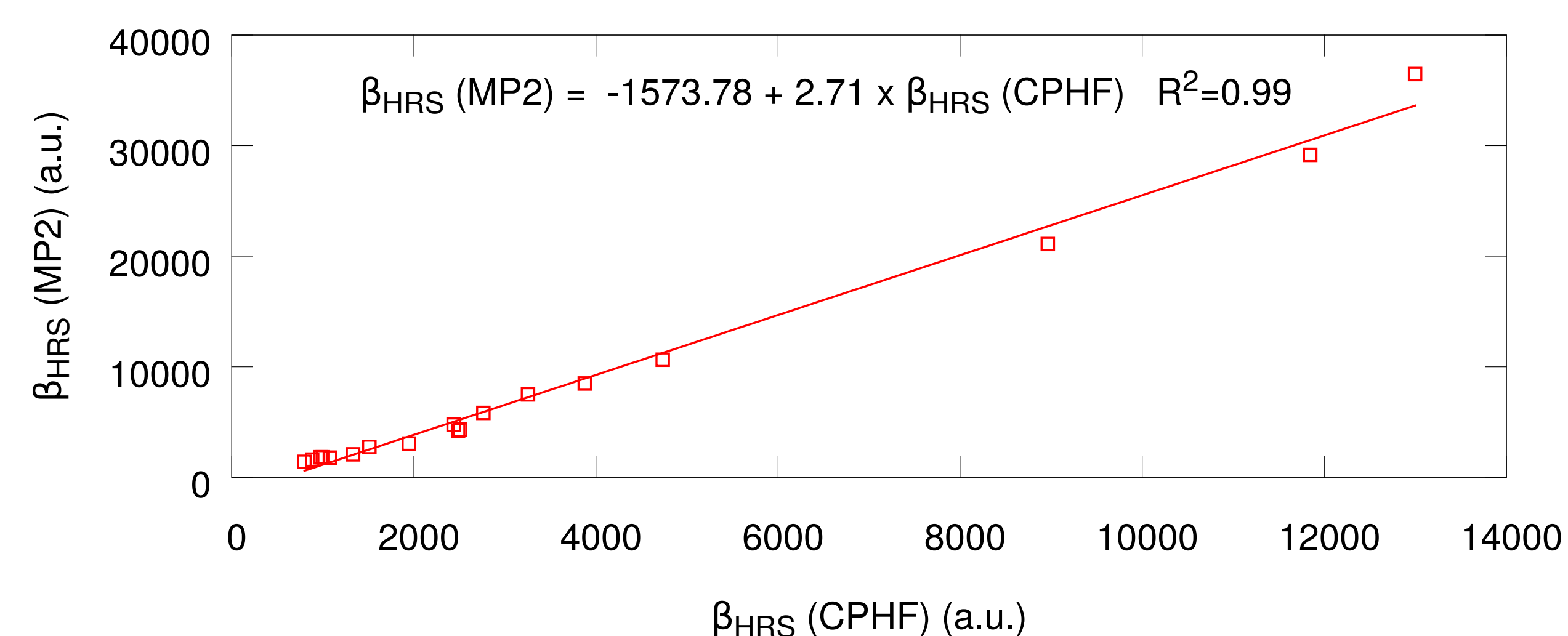


Figure: Effect of the inclusion of electron correlation on the static β_{HRS} of some oxazines (**3-4** and **6-12**), as estimated at the IEF-PCM/MP2 level of calculation

- Attractor substituents on the oxazines lead to smaller β_{HRS} contrast ratios.
- Donor substituents show larger contrast ratios.
- Compounds **5**, **8**, and **12** demonstrate appreciable contrasts in comparison to references NLO switches (**1** and **2**)
- **11** has a large NLO response for both forms.
- Inclusion of electron correlation increases β_{HRS} of 170 %

Computational details

- Optimization: M06/6-311G(d)
- First hyperpolarizabilities: Static (CPHF and MP2 with a finite field, FF, approach) and dynamic ($\lambda=1064$ nm, TDHF) with the 6-311+G(d) basis set
- Solvent effects on all calculations: IEF-PCM, in acetonitrile

Acknowledgements

All calculations were performed using the Gaussian 09 package⁶ as well as homemade code to carry out the FF (Romberg) scheme. Computational resources have been provided by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifique (F.R.S.-FNRS) under the Grant No. 2.5020.11.

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